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DATE: October 17, 2001

SUBJECT: WH&S BRANCH ACTIVITIES AND RESULTS OF ANALYSES RELATED TO THE INVESTIGATION OF 22-TUL-00 (PROJECT 0001) (1)

Incident Chronology

On June 9, 2000, a crew of 24 female field workers tying vines in a young vineyard were drifted upon by an aerial application of Lorsban®-4E (2 qt/acre; EPA registration number 400-82, 44.9% active ingredient chlorpyrifos) and Omite® 30 WS (2 lb/ac; EPA registration number 62719-220, 32% active ingredient propargite). The incident occurred in Tulare County, at the northwest corner of Avenue 120 and Road 184, where the crew had been working since June 5. The application was made by helicopter to 120 acres of almonds immediately west of the vineyard. At the time of the incident, some of the crew were working in the northwest section of this corner and some were working toward the center of the field (east).

The crew began work in the vineyard at 6 AM. Each crew member wore clothing which included face scarves and hats in addition to long-sleeved shirts, long pants, shoes and socks. Some crew members also wore a jacket. They saw the helicopter in the almonds between 6 AM and 8 AM. While none of crew reported feeling spray mist, many noted a strong chemical odor.

At 7 AM, the permit applicator for the almond application requested that the tying crew move further east in the vineyard. The crew moved to the west side of the eastern block of the vineyard. When members of the crew began feeling ill, the crew moved to the east side of the eastern block of the vineyard. At 8:45 AM, the crew left that vineyard to work at another location. While in transit, several more crew members developed illness symptoms. The crew was then transported to Delano Regional Medical Center, where all crew members reported symptoms which included nausea, vomiting, headache, dizziness and/or fainting, weakness, shakiness and/or tingling, eye irritation, and skin irritation. The systemic symptoms are compatible with over-exposure to chlorpyrifos, an organophosphate pesticide, and the irritation symptoms are compatible with over-exposure to propargite (2,3). The workers were decontaminated, submitted blood and urine samples, and were treated, and released.

Workers continued to experience symptoms and sought follow-up treatment. On June 12, 22 workers returned to Delano Regional Medical Center for treatment and submitted a second urine sample for analysis. Crew members were initially released to either restricted or full work duties between June 26 and July 7. Restrictions included wearing a hat and eye protection, drinking liquids freely and discontinuing working when the temperature was over 100 °F. However, 21 workers continued to experience persistent symptoms, including headache, fatigue, weakness, skin and eye irritation, blurred vision, stomach pain, vomiting, diarrhea, and shortness of breath. They continued to seek medical treatment and were not released to full work duties until July 20.

Also on June 9, two of the Delano Regional Medical Center staff who assisted in treating the workers prior to their being decontaminated developed illness symptoms compatible with over-exposure to chlorpyrifos and propargite. One female developed stomach cramps, nausea, and sweating 1.5 hours after the workers arrived at the hospital. She also reported a strong, irritating smell outside the emergency room where the workers were treated. The second staff person, also female, reported an itchy and sore throat, nausea, and irritated, watery eyes about 30 minutes after the fieldworkers arrived at the hospital. When these women developed symptoms, many of the hospital staff who had been in contact with the workers became concerned about secondary exposure. Altogether, 20 hospital staff and 24 workers submitted urine samples on June 9, and 22 workers submitted urine samples on June 12, for a total of 66 urine samples.

On-site Investigation and Sampling

The Tulare CAC was informed of the incident while the workers were at the hospital, where CAC investigators collected 4 shirts from crew members. Bernie Hernandez, of DPR/WH&S, assisted Tulare CAC staff in collecting dislodgeable foliar residue samples (DFR), and transported the DFR, clothing, and urine samples to the CDFA Center for Analytical Chemistry in Sacramento. Bernie collected twelve DFR samples, 10 grape and 2 almond, on June 9, between 1800 – 2000 hours. He noted a pesticidal odor throughout the sampling, which was quite strong in the almonds. Each grape sample consisted of 40 1-inch diameter punches (400 $cm^2$), with one leaf disc collected from each of 40 vines, collected on a gradient from west to east (4-6). Six samples were collected from the area where the tying crew was working in the block of grapes nearest to the almonds (west) and four samples were collected from the block where workers were tying vines furthest from the almonds (east). Two random samples were collected from the almonds, in a gradient from southeast to northwest, nearest to the crew's location in the grapes. Almond samples were collected by snipping whole leaves into sampling jars; leaf area was determined following sample analysis (7). Samples were collected, labeled, transported and transferred in accordance with applicable WH&S SOPs.

*DFR Sample Analysis* - Surface residues were dislodged with a 0.05% sodium sulfosuccinate solution and extracted with ethyl acetate. Chlorpyrifos analyses were conducted by GC-MSD on June 12. Propargite analyses were conducted by LC –UV on June 15. Results were reported as μg/sample. Results were divided by sample surface area for units of $\mu g/cm^2$. DFR results, presented in Table 1, confirm drift of both pesticides at low levels in the grape vineyard.

Table 1. Dislodgeable Foliar Residues ($\mu g/cm^2$) of Chlorpyrifos and Propargite on Grape and Almond Leaves in Priority Episode 22-TUL-00

| Crop, Block | $\mu g/cm^2$ chlorpyrifos | $\mu g/cm^2$ propargite |
|---|---|---|
| Grapes – West | 0.01 | 0.03 |
| | 0.01 | 0.03 |
| | 0.02 | 0.03 |
| | 0.01 | 0.03 |
| | 0.11 | 0.09 |
| | 0.03 | 0.04 |
| Grapes – East | ND[a] | 0.05 |
| | ND | 0.02 |
| | ND | 0.05 |
| | ND | 0.02 |
| Almonds | 2.32 | 1.21 |
| | 1.38 | 1.06 |

a ND - None detected; limit of quantitation = 0.003 $\mu g/cm^2$ chlorpyrifos

*Clothing Samples* – The four shirts were analyzed on June 15 for residues of chlorpyrifos and propargite. Propargite was not detected on any shirt (limit of detection = 20 – 30 μg/sample). Chlorpyrifos was found on two shirts at 25 and 69 μg, respectively (limit of detection = 15 μg/sample). These results also confirm that drift occurred.

*Urine Samples* – Urinalyses for 3,5,6-trichloropyridinol (3,5,6-TCP) were conducted between June 29 and July 20, using a GC equipped with a mass spectrometer detector (HP 6890/MSD) (8). Results were reported as ppb 3,5,6-TCP with a limit of detection of 4 ppb. Results and analytical recoveries are summarized in Table 2. The results for exposed workers show similar average and standard deviations for 3,5,6-TCP levels on both sampling dates. Hospital staff had average urinary 3,5,6-TCP present at 2 - 3 times the workers' levels.

Table 2. Urinary 3,5,6-Trichloropyridinol (ppb) for 24 Workers Exposed to Chlorpyrifos Drift and 20 Hospital Workers in Priority Episode 22-TUL-00

| | | ppb 3,5,6-TCP (limit of detection = 4 ppb) | | |
|---|---|---|---|---|
| Sample Identity | Date Collected | Mean | Standard Deviation | Count of Samples |
| Exposed Workers | 6/9/00 | 4.01 | 5.08 | 24 |
| | 6/12/00 | 5.35 | 3.16 | 20 |
| Hospital Staff | 6/9/00 | 10.72[a] | 14.59 | 22 |
| Quality Assurance Recoveries | | | | |
| Fortification Levels | % Recovery | Mean | Standard Deviation | Count of Samples |
| 10 ppb 3,5,6-TCP | 72.37 | 7.24 ppb | 1.84 ppb | 10 |
| 50 ppb 3,5,6-TCP | 108.78 | 54.39 ppb | 8.06 ppb | 8 |

a skewed by a single sample of 65 ppb 3,5,6-TCP. Excluding this sample yields a mean of 7.9 $\pm$ 7.2 ppb 3,5,6-TCP.

While drift was confirmed, the urinalysis results may not provide much information regarding the workers' exposure. Generally, accumulative collections of urine for 72 hours would represent approximately 62% of the total 3,5,6-TCP absorbed dose (2). Less information can be presumed from the two spot samples, collected at 8 – 10 hours and 72 hours post-exposure, respectively. A recent study by Hill et al. indicates that 82% of the US population has measurable concentrations of 3,5,6-TCP, which is likely related to frequent use of chlorpyrifos in residential and structural pest control applications (9). The exposed vineyard workers showed urinary excretion of 3,5,6-TCP equivalent to the mean background level of 4.5 ppb found in the above study. The crew's absorption of chlorpyrifos was likely minimal. Factors that mitigated absorption included the crew's wearing work clothing, which covered all body areas except the face, and being decontaminated within 3 hours of exposure. The clothing penetration rate for chlorpyrifos averages 7.8% (2). Given the small amounts of chlorpyrifos recovered from the workers' clothing, it was unlikely that workers absorbed more than a few micrograms. Such amounts would be unlikely to be detected above background 3,5,6-TCP levels, especially in a spot sample.

The mean 3,5,6-TCP level for the hospital workers was far greater than the workers'. Their mean 3,5,6-TCP excretion (10.72 ppb) approximates the 90$^{th}$ percentile in the Hill study (9.5 ppb); the upper bound of the standard deviation for hospital staff approaches the 99$^{th}$ percentile in the Hill study (27 ppb). However, this average was skewed by a single hospital staff sample of 65 ppb 3,5,6-TCP. The worker did not report any illness symptoms. Excluding this result yields an adjusted mean of 7.9 $\pm$ 7.2 ppb 3,5,6-TCP. Overall, seven hospital workers had levels greater than 8 ppb 3,5,6-TCP, with six of the seven high samples between 11.6 and 18.8 ppb 3,5,6-TCP. Hospital staff may have been secondarily exposed to chlorpyrifos residues present on the workers and their clothing prior to decontamination.

*Blood Samples* – All workers' blood tests indicated cholinesterase levels were in the normal range.

*Follow-up Investigation* – The vineyard owner wanted to know when workers would be able to complete the vine tying. Dr. Michael O'Malley, of WH&S, summarized the worker safety issues in a memo dated June 16, 2000 (10). The highest DFR residues were approximately 0.1 $\mu g/cm^2$ for both propargite and chlorpyrifos. This level might be of marginal concern for repeated exposures from a high contact work activity such as harvesting in a fully mature canopy. However, the canes in this vineyard were young, with few leaves, and tying is a low contact activity. In addition, residues had decayed over the week since the drift incident occurred. Thus, Dr. O'Malley determined that the vineyard was unlikely to represent a hazard. Based on this determination, the field was released without any restrictions on June 16.

*Violations, Compliance and Enforcement Actions* – The investigation determined that several violations of Title 3, California Code of Regulations (3 CCR) (11) and the Food and Agriculture Code (FAC) (12) occurred and Violation Notices were issued for the following noncompliances:

1. The property owner failed to post the Omite® 30WS application every 600 feet along the public right-of-way and in the northeast corner of the almond orchard (3CCR 6776(d)).
2. The pest control advisor (PCA) was not registered with the Tulare CAC when he made his written recommendations (FAC 12002) and his recommendation incorrectly specified a 7-day restricted entry interval (REI) for Omite® 30WS instead of the required 21-day REI (FAC 12002, 3 CCR 6556(c)).
3. The farm labor contractor did not take his employees to the doctor (3 CCR 6766(c)).
4. The aerial application firm did not use Omite® 30 WS and Lorsban®-4E in complete compliance with rules and regulations, did not apply the two pesticides in a safe and effective manner, and continued the application when both chemicals drifted from the application site to nontarget private property, which resulted in 24 farmworkers seeking medical treatment, and prevented normal use of the vineyard owner's grapes (FAC 12991(e), 3 CCR 6600(b), 6614(b)(1), 6614(b)(3)).

5. The applicator applied Omite® 30 WS and Lorsban®-4E in a faulty manner, failed to prevent substantial drift of both pesticides, and caused contamination of Omite® 30WS to workers' clothing (FAC 11791(b), 12972, 12973).

Violations 1 – 3 did not contribute to the incident. Violations 4 and 5 did contribute directly to the incident and resulted in the Agricultural Civil Penalties (ACPs) listed below. The Tulare CAC issued ACPs with total fines of $3,965, as follows:

- A fine of $2,000 was issued to aviation firm which made the application for failure to apply Omite® 30WS in a safe and effective manner, failure to exercise reasonable precautions to avoid environmental contamination, and failure to prevent substantial drift (3 CCR 6600(b), 6600(e), 6614(b)).
- A fine of $1,965 was issued to the pilot who made the application for allowing drift of Omite® 30WS and Lorsban®-4E to nontarget areas and use of both products in conflict with labeling or other applicable limitations (FAC 12972, 12973).

References

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11. California Department of Pesticide Regulation (1998) Title 3, Division 6, California Code of Regulations. California Department of Pesticide Regulation, 1001 I Street, Sacramento, California 95814
12. California Food and Agriculture Code, Office of Administrative Law, available on their web site at: http://www.oal.ca.gov (accessed September 4, 2001)